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(54) **High performance epoxy adhesive.**

(57) The present invention relates to a two component epoxy adhesive system comprising an epoxy component comprising (1) at least one aromatic multifunctional epoxy resin; and a hardener component comprising (1) a polyamide of a dimer fatty acid, (2) at least one aliphatic or cycloaliphatic amine and (3) at least one aromatic amine; and wherein CR a polyglycidyl ether of sorbitol, having more than 2 oxirane groups per molecule, as an accelerator is present in the epoxy component and/or a tertiary amine accelerator is present in the hardener component.

EP 0 488 949 A2

The present invention relates to a two component epoxy adhesive system comprising an epoxy resin component and a hardener component.

The use of epoxide resins in adhesives has been commercial practice for several decades. Many hardeners for epoxy resins are reactive at room temperature and so need to be mixed with the epoxide just prior to use. Others are stable in admixture with the epoxide resin at room temperature, and harden only when heated to elevated temperatures. These hardeners, the so-called "latent hardeners" or "latent curing agents" are available commercially and include dicyandiamide and polycarboxylic acid hydrazides.

Compositions containing an epoxide resin and such a latent hardener generally take about 15 minutes to 1 hour to cure at temperatures of about 180°C. Cure times can be shortened by incorporation of accelerators. An accelerator which is often used when compositions having good impact resistance and heat resistance are required, for example in certain adhesive pastes for the automotive industry, is benzimidazole. However, compositions containing benzimidazole as the accelerator have undesirably limited storage stabilities at ambient temperature.

Accordingly, it is a primary object of the present invention to provide an epoxy adhesive system which exhibits good impact resistance, good heat resistance and prolonged storage stability at ambient temperature and can cure rapidly at both ambient and elevated temperatures.

A further object of the present invention is to provide a flexible, yet thermally resistant adhesive with high peel strength and ability to bond to a variety of substrates.

Various other objects and advantages of the present invention will become apparent from the following description thereof.

The present invention relates to a two component epoxy adhesive system comprising an epoxy component comprising (1) at least one aromatic multifunctional epoxy resin; and a hardener component comprising (1) a polyamide of a dimer fatty acid, (2) at least one aliphatic or cycloaliphatic amine and (3) at least one aromatic amine; and wherein a polyglycidyl ether of sorbitol, having more than 2 oxirane groups per molecule, as an accelerator is present in the epoxy component and/or a tertiary amine accelerator is present in the hardener component.

The present invention provides a two component epoxy adhesive system comprising:

(A) an epoxy component comprising:

(1) at least one aromatic multifunctional epoxy resin; and

(B) a hardener component comprising:

(1) a polyamide of a dimer fatty acid,

(2) at least one aliphatic or cycloaliphatic amine and

(3) at least one aromatic amine; and

wherein a polyglycidyl ether of sorbitol, having more than 2 oxirane groups per molecule, as an accelerator is present in the epoxy component and/or a tertiary amine accelerator is present in the hardener component.

#### The Epoxy Resin Component

Suitable aromatic multifunctional epoxy resins for use in the epoxy resin component are virtually all aromatic epoxy resins containing on average at least two 1,2-epoxy groups per molecule.

Illustrative examples of such aromatic multifunctional epoxy resins are:

Polyglycidyl and poly( $\beta$ -methylglycidyl) ethers which may be obtained by reacting a compound containing at least two phenolic hydroxyl groups in the molecule with epichlorohydrin, glycerol dichlorohydrin or with  $\beta$ -methyl epichlorohydrin under alkaline conditions or in the presence of an acid catalyst, and subsequent treatment with an alkali. Illustrative of compounds containing at least two phenolic hydroxyl groups in the molecule are alcohols containing aromatic groups such as N,N-bis(2-hydroxyethyl)aniline or p,p'-bis(2-hydroxyethylamino)diphenylmethane; or mono- or polynuclear polyphenols such as resorcinol, hydroquinone, bis(4-hydroxyphenyl)methane,

2,2-bis(4-hydroxyphenyl)propane, brominated 2,2-bis(4-hydroxyphenyl)propane, bis(4-hydroxyphenyl) ether, bis(4-hydroxyphenyl)sulfone,

1,1,2,2-tetrakis(4-hydroxyphenyl) ethane or novolaks which are obtainable by condensation of aldehydes such as formaldehyde, acetaldehyde, chloral or furfuraldehyde with phenols or alkyl- or halogen-substituted phenols such as phenol, the above described bisphenols, 2- or 4-methylphenol, 4-tert-butylphenol, p-nonylphenol or 4-chlorophenol.

Poly(N-glycidyl) compounds which may be obtained by dehydrochlorinating the reaction products of epichlorohydrin with amines which contain at least two amino hydrogen atoms. Amines from which these epoxy resins are derived are, typically, aromatic amines such as aniline, p-toluidine, bis(4-aminophenyl) methane,

bis(4-aminophenyl) ether, bis(4-aminophenyl)sulfone, 4,4'-diaminobiphenyl or 3,3'-diaminobiphenyl; or araliphatic amines such as m-xylylenediamine.

Poly(S-glycidyl) derivatives, for example bis(S-glycidyl) derivatives which are derived from bis(4-mercaptomethylphenyl) ether.

It is also possible, however, to use epoxy resins in which the 1,2-epoxy groups are attached to different hetero atoms or functional groups. These compounds, comprise, for example, the N,N,O-triglycidyl derivative of 4-aminophenol, the N,N,O-triglycidyl derivative of 3-aminophenol or the glycidyl ether/glycidyl ester of salicylic acid.

Preferred aromatic multifunctional epoxy resins include N,N,O-triglycidyl-4-aminophenol, N,N,N',N'-tetraglycidyl derivative of methylene dianiline, epoxidized novolaks, epoxidized bisphenol A resins, epoxidized resorcinol and epoxidized bisphenol F. Most preferably, N,N,O-triglycidyl-4-aminophenol is used.

The aromatic multifunctional epoxy resin is present in a range of from about 5 to about 60 wt%, preferably about 7 to about 30 wt%, most preferably about 10 to about 20 wt% based upon the total weight of the epoxy component.

Additionally, the epoxy resin component may further contain an aliphatic multifunctional epoxy resin. Suitable aliphatic multifunctional epoxy resins for use in the epoxy resin component are virtually all aliphatic epoxy resins containing on average at least two 1,2-epoxy groups per molecule.

Illustrative examples of such aliphatic multifunctional epoxy resins are:

Polyglycidyl and poly( $\beta$ -methylglycidyl) esters which may be obtained by reacting a compound containing at least two carboxyl groups in the molecule with epichlorohydrin, glycerol dichlorohydrin or with  $\beta$ -methylepichlorohydrin in the presence of a base. Illustrative of compounds containing at least two carboxyl groups in the molecule are saturated aliphatic dicarboxylic acids such as adipic acid or sebacic acid; or unsaturated aliphatic dicarboxylic acids such as maleic acid; or aromatic dicarboxylic acids such as phthalic acid, isophthalic acid or terephthalic acid; or copolymers of (meth)acrylic acid with copolymerisable vinyl monomers such as the 1:1 copolymers of methacrylic acid with styrene or with methylinethacrylate.

Polyglycidyl and poly( $\beta$ -methylglycidyl) ethers which may be obtained by reacting a compound containing at least two alcoholic hydroxyl groups in the molecule with epichlorohydrin, glycerol dichlorohydrin or with  $\beta$ -methyl epichlorohydrin under alkaline conditions or in the presence of an acid catalyst, and subsequent treatment with an alkali. Illustrative of compounds containing at least two alcoholic hydroxyl groups in the molecule are aliphatic alcohols such as ethylene glycol, diethylene glycol and higher poly(oxyethylene) glycols, 1,2-propanediol, 1,3-propanediol or poly(oxypropylene) glycols, 1,4-butanediol or poly(oxybutylene) glycols, 1,5-pentanediol, neopentyl glycol (2,2-dimethylpropanediol), 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol or 1,12-dodecanediol; 2,4,6-hexanetriol, glycerol, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, pentaerythritol, sorbitol or polyepichlorohydrins; or cycloaliphatic alcohols such as 1,3- or 1,4-dihydroxy-cyclohexane, 1,4-cyclohexanedimethanol, bis(4-hydroxycyclohexyl)methane, 2,2-bis-(4-hydroxycyclohexyl)propane or 1,1-bis(hydroxymethyl)cyclohex-3-ene;

Poly(N-glycidyl) compounds which may be obtained by dehydrochlorinating the reaction products of epichlorohydrin with amines which contain at least two amino hydrogen atoms. Amines from which these epoxy resins are derived are, typically, aliphatic amines such as hexamethylenediamine or n-butylamine.

Included among the poly(N-glycidyl) compounds are also triglycidyl isocyanurate, N,N'-diglycidyl derivatives of cycloalkyleneureas, for example of ethyleneurea or of 1,3-propyleneurea, and N,N'-diglycidyl derivatives of hydantoins, for example of 5,5-dimethylhydantoin.

Poly(S-glycidyl) derivatives, for example bis(S-glycidyl) derivatives which are derived from dithiols such as 1,2-ethanedithiol.

Cycloaliphatic epoxy resins or epoxidation products of dienes or polyenes, such as cycloaliphatic epoxy resins which may be prepared by epoxidation of ethylenically unsaturated cycloaliphatic compounds. Illustrative of such compounds are 1,2-bis(2,3-epoxycyclopentyl)oxyethane, 2,3-epoxycyclopentyl glycidyl ether, diglycidyl esters of cyclohexane-1,2-dicarboxylic acid, 3,4-epoxycyclohexyl glycidyl ether, bis(2,3-epoxycyclopentyl)ether, bis(3,4-epoxycyclohexyl)ether, 5(6)-glydiyl-2-(1,2-epoxyethyl)bicyclo[2.2.1]heptane, dicyclopentadiene dioxide, cyclohexa-1,3-diene dioxide, 3,4-epoxy-6-methylcyclohexylmethyl-3',4'-epoxy-6'-methylcyclohexanecarboxylate or 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate.

It is also possible, however, to use epoxy resins in which the 1,2-epoxy groups are attached to different hetero atoms or functional groups. These compounds comprise, for example, N-glycidyl-N'-(2-glycidylloxypopyl)-5,5-dimethylhydantoin or 2-glycidyl-1,3-bis-(5,5-dimethyl-1-glycidylhydantoin-3-yl)propane.

Preferred aliphatic multifunctional epoxy resins include diglycidylesters of cyclohexane-1,2-dicarboxylic acid, trimethylol ethane triglycidyl ether and trimethylol propane triglycidyl ether. Most preferably trimethylol propane triglycidyl ether is used.

The aliphatic multifunctional epoxy resin is present in a range of from about 10 to about 75 wt%, preferably

about 10 to about 50 wt%, most preferably about 12 to about 20 wt% based upon the total weight of the epoxy component.

The preparation of the polyglycidyl ether of sorbitol, having more than 2 oxirane groups per molecule, is described in U.S. Patent No. 4,914,164, which is hereby incorporated by reference. If the polyglycidyl ether of sorbitol, having more than 2 oxirane groups per molecule, is used it is present in a range of from about 5 to about 50 wt%, preferably about 10 to about 30 wt%, most preferably about 12 to about 20 wt% based upon the total weight of the epoxy component.

The epoxy resin component may also contain other conventional modifiers such as extenders, fillers and reinforcing agents, pigments, dyestuffs, organic solvents, plasticizers, tackifiers, rubbers, diluents, adhesion promoters, such as epoxy silane, and the like. As extenders, reinforcing agents, fillers and pigments which can be employed in the epoxy resin component according to the invention there may be mentioned, for example: glass fibers, glass balloons, boron fibers, carbon fibers, cellulose, polyethylene powder, polypropylene powder, mica, quartz powder, gypsum antimony trioxide, bentonites, talc, silica aerogel ("Aerosil"), fumed silica, wollastonite, silane treated wollastonite, lithopone, barite, calcium carbonate, titanium dioxide, carbon black, graphite, iron oxide, or metal powders such as aluminum powder or iron powder. The preferred fillers are fumed silica, wollastonite and silane treated wollastonite. It is also possible to add other usual additives, for example, agents for conferring thixotropy, flow control agents such as silicones, cellulose acetate butyrate, polyvinyl butyral, stearates and the like.

Preferably, the epoxy resin component includes one or more fillers selected from the group consisting of aluminum powder, Wollastonite, silane treated Wollastonite and fumed silica in an amount ranging from about 1 to about 50 wt%, preferably about 1.5 to about 40 wt%, most preferably about 2.00 to about 38 wt% based upon the total weight of the epoxy component. More preferably, the epoxy component further comprises an epoxy silane as an adhesion promoter which provides the cured adhesive with resistance to moisture and is present in an amount of from about 0.25 to about 6.0 wt%, preferably about 0.4 to about 1.5 wt%, most preferably about 0.5 to about 1.0 wt% based upon the total weight of the epoxy component.

#### The Hardener Component

Suitable polyamides of a dimer fatty acid include a hydrogenated polyaminoamide (VERSAMID® 140, Henkel), a conventional polyamide (UM-REZ® 2188, Union Camp), VERSAMID® 125 (Henkel), VERSAMID® 115 (Henkel) and HY 840® (CIBA-GEIGY). Preferably, VERSAMID® 140 (Henkel) is used. Polyamidoamines are prepared by dimerizing tall oil fatty acids and then reacting the dimerized acid with aliphatic amines such as diethylenetriamine. These hardeners are described by V. Brytus, Modern Paint and Coatings, Vol. 74, No. 10, p. 172 (1984).

The polyamide of a dimer fatty acid is present in a range of from about 5 to about 55 wt%, preferably about 7 to about 43 wt%, most preferably about 20 to about 35 wt% based upon the total weight of the hardener component.

Suitable aliphatic or cycloaliphatic amines for use in the hardener component include monoethanolamine, N-aminoethyl ethanol amine, ethylenediamine, hexamethylenediamine, trimethylhexamethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, N,N-dimethylpropylenediamine-1,3, N,N-diethylpropylenediamine-1,3, bis(4-amino-3-methylcyclohexyl)methane, bis(p-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)propane, N-aminoethyl-piperazine, 1,3-diaminocyclohexane, 1,4-diaminocyclohexane, 1,3-bis(aminomethyl)cyclohexane, isophorone diamine and 3,5,5-trimethyl-s-(aminomethyl)-cyclohexylamine.

Preferred aliphatic or cycloaliphatic amines include bis(p-aminocyclohexyl)methane, N,N-dimethylpropylene diamine-1,3, isophorone diamine and diethylenetriamine. Most preferably, N,N-dimethylpropylene diamine-1,3 or bis(p-aminocyclohexyl)methane is used.

The aliphatic or cycloaliphatic amine is present in a range of from about 5 to about 90 wt%, preferably about 6.0 to about 20 wt%, most preferably about 7 to about 15 wt% based upon the total weight of the hardener component.

Suitable aromatic amines include m-phenylene-diamine, p-phenylenediamine, bis(p-aminophenyl)methane, bis(p-aminophenyl)sulfone, m-xylylenediamine, toluene diamine, 4,4'-methylene-dianiline, a diaminodiphenylether, benzidine, 4,4'-thiodianiline, 4-methoxy-6-m-phenyldiamine, 2,6-diaminopyridine, dianisidine and 1-methyl-imidazole.

Preferred aromatic amines include M-xylylenediamine, 4,4'-methylene dianiline and bis(p-aminophenyl)sulfone. Most preferably, methylene dianiline or m-xylylenediamine is used.

The aromatic amine is present in a range of from about 5 to about 70 wt%, preferably about 5 to about 50 wt%, most preferably about 7 to about 20 wt% based upon the total weight of the hardener component.

Suitable tertiary amine accelerators include triethylamine, tris(dimethylaminoethyl)phenol, boron trif-

fluoride-amine complex, benzyl dimethylamine and 2-(dimethylaminomethyl)phenol. Preferably, tris(dimethylaminoethyl)phenol is used.

If the tertiary amine accelerator is used it is present in a range of from about 0.5 to about 7 wt%, preferably about 1 to about 5 wt%, most preferably about 1.5 to about 3.5 wt% based upon the total weight of the hardener component.

The hardener component may also contain other conventional modifiers such as extenders, fillers and reinforcing agents, pigments, dyestuffs, organic solvents, plasticizers, tackifiers, rubbers, diluents, adhesion promoters, such as epoxy silane, toughening agents, such as an amino terminated acrylonitrile/butadiene copolymer, coupling agents, such as amino silane and the like. As extenders, reinforcing agents, fillers and pigments which can be employed in the epoxy resin component according to the invention there may be mentioned, for example: glass fibers, glass balloons, boron fibers, carbon fibers, cellulose, polyethylene powder, polypropylene powder, mica, quartz powder, gypsum, antimony trioxide, bentonites, talc, silica aerogel ("Aerosil"), fumed silica, wollastonite, silane treated wollastonite, lithopone, barite, calcium carbonate, titanium dioxide, carbon black, graphite, iron oxide, or metal powders such as aluminum powder or iron powder. The preferred fillers are fumed silica, wollastonite and aluminum powder. It is also possible to add other usual additives, for example, agents for conferring thixotropy, flow control agents such as silicones, cellulose acetate butyrate, polyvinyl butyral, stearates and the like.

Additionally, a surfactant can be used such as a fluoropolymer surfactant, titanates and zirconates. Preferably, the hardener component contains a fluoropolymer surfactant in an amount ranging from about 0.10 to about 3.0 wt%, preferably about 0.25 to about 1.0 wt%, most preferably about 0.25 to about 0.50 wt% based upon the total weight of the hardener component.

Preferably, the hardener component includes one or more fillers selected from the group consisting of aluminum powder, Wollastonite and fumed silica in an amount ranging from about 0.5 to about 40 wt%, preferably about 1 to about 30 wt%, most preferably about 1.5 to about 15.0 wt% based upon the total weight of the epoxy component.

The mix ratio of the epoxy resin component to the hardener component is about 1 to about 0.15 by weight, preferably about 1 to about 0.5 by weight, most preferably about 1 to about 0.7 by weight.

A vertical type high-speed agitator, kneading machine, roll machine, ball mill or any other suitable mixing and agitating machine may be used for dispersion of the components of the composition of the present invention.

The invention also provides a method of bonding or sealing two surfaces together which comprises applying a composition of the invention to one or both surfaces, placing the two surfaces together with the composition positioned therebetween and, permitting the adhesive to cure at from about room temperature to about 121°C. Preferably, a room temperature cure is employed. This method may be used with surfaces of metal, such as steel or aluminum, plastic materials, glass, friction materials, such as brake linings, and ceramic materials.

The following examples serve to give specific illustrations of the practice of this invention but they are not intended in any way to limit the scope of this invention.

#### EXAMPLE 1

This example illustrates the preparation, physical properties, mechanical properties and durability testing of a typical composition of the present invention. The ingredients are listed in Table 1 and the physical and mechanical properties are listed in Tables 2 to 4, respectively.

Table 1

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Epoxy Resin Component

	<u>Ingredient</u>	<u>Content (wt. %)</u>
10	Bisphenol A Epoxy Resin (XU GY 6010 from CIBA-GEIGY Corp.)	47.50
15	Epoxy resin of Sorbitol (XU GY 358 from CIBA-GEIGY Corp.)	12.50
	Epoxy resin of p-aminophenol (MY 0510 from CIBA-GEIGY Corp.)	15.00
20	Epoxy silane (Silane A-187 from UNION CARBIDE)	0.50
	Aluminum powder	10.00
25	Wollastonite (Wollastonite P-4 from NYCO)	12.50
	Fumed Silica (CABOSIL® TS 720 from Cabot Corp.)	2.00

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Hardener Component

5	<u>Ingredient</u>	<u>Content (wt. %)</u>
	Polyamide of C <sub>18</sub> fatty acids (VERSAMID® 140 CE from Henkel)	22.92
10	Amine adduct of MY 0500 (CIBA-GEIGY) (HY 355 from CIBA-GEIGY Corp.)	12.73
	3-Dimethylaminopropylamine	7.15
15	Amino terminated acrylonitrile/butadiene copolymer (ATBN 1300x16 from BF GOODRICH)	49.95
20	Tris(dimethylamino)phenol (DY 064 from CIBA-GEIGY Corp.)	3.00
	Amino silane (Silane A-1102 from UNION CARBIDE)	1.50
25	Fluoropolymer surfactant (FLUORAD® FC-430 from 3M Corp.)	0.25
30	Fumed Silica (CABOSIL® M-5 from CABOT Corp.)	2.50

Table 2Physical Properties

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Mix Ratio	100:100 (pbv) 100:70 (pbw)
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Viscosity (Brookfield RVF, 75°F Resin, Spindle #6 at 4 RPM Hardener, Spindle #6 at 4 RPM Mixed, Spindle #6 at 4 RPM)	91,250 cps 102,000 cps 53,750 cps
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Gel Time (dry wire method)	55 minutes
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Tensile Strength (ASTM D638)	4634 psi
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Elongation at Break (ASTM D638)	11.0%
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Tensile Modulus (ASTM D638)	212,000 psi
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Glass Transition Temperature (Rheometrics)	77°C and 110°C
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Cure	7 Days/77°F
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Mix ratio of epoxy resin component and hardener component is 1:1 by volume.	
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Either bare or clad (0.160 cm) aluminum 2024-T3 alloy (available from Copper and Brass Sales) was used as the substrate for mechanical tests, other than T-peels. All aluminum was etched as per ASTM D2651, method A (chromic acid). All samples were cured at 25°C for 7 days prior to testing, and lap shear specimens were tested according to ASTM D1002. Bondline thickness was maintained at 0.010-0.013 cm. In the exposure tests, Federal Specification MMM-A-132A procedures were followed. Testing temperatures for lap shears were also done in accordance with the above specification.

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Table 3Mechanical PropertiesAluminum Bonding  
TemperatureLap Shear Strength  
Bare                      Clad-67°F

3520 psi

3330 psi

77°F

4310 psi

4340 psi

180°F

2570 psi

2580 psi

ASTM D1002; Aluminum etched per ASTM D2651, Method A.

T-Peel (77°F; ASTM D1876, 0.010" bondline)

7 pli

Thermoplastic Bonding  
Substrate

## Lap Shear Strength

Ultem 1000 (Polyetherimide from  
GENERAL ELECTRIC)

1370 psi (SF)

Ryton R-5 (Polyphenylene sulfide  
from PHILLIPS PETROLEUM)

522 psi (SF)

Cured 190°F/1.5 hr. Ultem-Dry wipe only before applying adhesive. Ryton R-5-Chromic  
acid etched before applying adhesive. 0.020" bondline, 1.0" overlap. SF=Substrate  
Failure.Table 4Durability Testing

Fatigue (ASTM D3166)

750 psi at  $1 \times 10^6$  cycles, 3600 cpm

Pass

Fluid Immersion

JP-4 (7 Days/75°F)

Lap Shear Strength

4946 psi

Humidity Exposure

30 Days 120°F at 97% RH

2630 psi

Thermal Aging

7 Days/180°F

4750 psi

7 Days/250°F

4110 psi

Bare 2024-T3 aluminum alloy, etched as per ASTM D2651, Method A. Testing at 75°F.

EXAMPLES 2-5

These examples further illustrate the preparation and mechanical properties of additional compositions of the present invention. The ingredients are listed in Table 5 and the mechanical properties are listed in Table 6.

Table 5Epoxy Resin Component

<u>Ingredient</u>	<u>Content (wt. %)</u>			
	<u>Ex.2</u>	<u>Ex.3</u>	<u>Ex.4</u>	<u>Ex.5</u>
Epoxy Resin of Sorbitol (GY 358)	-	10.0	20.0	30.0
Bisphenol A Epoxy Resin (GY 6010)	55.0	45.0	35.0	25.0
Epoxy Resin of p-aminophenol (MY 0510)	20.0	20.0	20.0	20.0
Epoxy Silane (Silane A-187)	0.5	0.5	0.5	0.5
Wollastonite (Wollastonite P-4)	18.5	18.5	18.5	18.5
Fumed Silica (CABOSIL® M-5)	6.0	6.0	6.0	6.0

Hardener Component (Examples 2-5)

<u>Ingredient</u>	<u>Content (wt. %)</u>
Polyamide of C <sub>18</sub> fatty acid (VERSAMID® 140 CE)	32.50
Aromatic Amine Adduct (XB 3075 from CIBA-GEIGY)	7.50
Dimethylaminopropylamine	5.0
Amino terminated acrylonitrile/butadiene copolymer (ATBN 1300x16 from Hycar Corp.)	20.00
Tris(dimethylamino)phenol (DY 064)	3.0
Amino Silane (Silane A-1102)	1.50
Fluoropolymer Surfactant (FLUORAD® FC-430)	0.25
Wollastonite (Wollastonite P-4)	15.50
Aluminum powder	9.75
Fumed Silica (CABOSIL® M-5)	5.00
The mix ratio of the epoxy resin component to the hardener component is 100/100 by weight.	

EXAMPLE 6

This example further illustrates the preparation and mechanical properties of a typical composition of the present invention. The ingredients are listed in Table 7 and the physical properties are listed in Tables 8.

Table 7Epoxy Resin Component

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IngredientContent (wt. %)

10

Bisphenol A Epoxy Resin  
(GY 6010 from CIBA-GEIGY Corp.)

47.50

Epoxy Resin of Sorbitol  
(GY 358 from CIBA-GEIGY Corp.)

12.50

15

Epoxy Resin of p-aminophenol  
(MY 0510 from CIBA-GEIGY Corp.)

15.00

Epoxy silane  
(Silane A-187 from UNION CARBIDE)

0.50

20

Aluminum powder

10.00

Wollastonite P-4  
(from NYCO)

12.50

25

Fumed silica  
(CABOSIL® TS 720 from Cabot Corp.)

2.00

30

35

40

45

50

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Hardener Component

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IngredientContent (wt. %)Polyamide of C<sub>18</sub> Fatty Acids  
(VERSAMID 140 from Henkel)

30.92

10

Amine adduct of MY 0500  
(HY 355 from CIBA-GEIGY Corp.)

14.73

Dimethylaminopropaneamine

7.15

15

Amino terminated acrylonitrile/butadiene  
copolymer  
(ATBN 1300x16 from B.F. GOODRICH)

39.95

Tris(dimethylamino)phenol  
(DY 064 from CIBA-GEIGY Corp.)

3.00

20

Amino silane  
(Silane A-1102 from UNION CARBIDE)

1.50

Fluoropolymer surfactant  
(Fluorad FC-430 from 3M Corp.)

0.25

25

Fumed silica  
(CABOSIL®M5 from Cabot Corp.)

2.50

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The mix ratio of the epoxy resin component to the hardener component is 1/1 by volume.

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Table 8

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Lap Shear Strength-67°F75°F180°F30 Days/120°F/97% RH

3490 psi

4674 psi

2182 psi

2940 psi

45

ASTM D1002, 7 day/77°F cure

50

T-Peel

12 pli

ASTM D1876, 7 day/77°F cure

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EXAMPLE 7

This example further illustrates the preparation and mechanical properties of a typical composition of the present invention. The ingredients are listed in Table 9 and the physical properties are listed in Tables 10.

Table 9Epoxy Resin Component

<u>Ingredient</u>	<u>Content (wt. %)</u>
Epoxy resin of MDA (methylene dianiline) (MY 721 from CIBA-GEIGY Corp.)	19.47
Epoxy novolac resin (EPN 1138 from CIBA-GEIGY Corp.)	11.72
Trimethylolpropane triglycidyl ether (Heloxy 5048 from HI-TEK POLYMERS)	7.85
Epoxy silane (A-187 from UNION CARBIDE)	0.51
Aluminum powder	37.41
Silane treated Wollastonite (400 Wollastokup 10222 from NYCO)	21.00
Fumed silica (CABOSIL® M5 from Cabot Corp.)	2.04

Hardener Component

<u>Ingredient</u>	<u>Component (wt. %)</u>
p-aminodicyclohexylmethane	80.00
Amine adduct of MY 0500 (HY 355 from CIBA-GEIGY Corp.)	10.00
Dimethylaminopropaneamine	5.25
Tris(dimethylamino)phenol (DY 064 from CIBA-GEIGY Corp.)	3.00
Amino silane (silane A-1102 from UNION CARBIDE)	1.50
Fluoropolymer surfactant (FLUORAD® FC-430 from 3M Corp.)	0.25

The mix ratio of the epoxy resin component to the hardener component is 100/16 by weight.

Table 10Lap Shear Strength

<u>-67°F</u> 1974 psi	<u>75°F</u> 2788 psi	<u>180°F</u> 2346 psi	<u>300°F</u> 1267 psi	<u>400°F</u> 508 psi
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ASTM D1002, 7 day/77°F cure

EXAMPLE 8

This example further illustrates the preparation and mechanical properties of a typical composition of the present invention. The ingredients are listed in Table 11 and the physical properties are listed in Tables 12.

Table 11Epoxy Resin Component

<u>Ingredient</u>	<u>Content (wt. %)</u>
Epoxy resin of MDA (methylene dianiline) (MY 721 from CIBA-GEIGY Corp.)	19.47
Epoxy novolac resin (EPN 1138 from CIBA-GEIGY Corp.)	11.72
Epoxy resin of p-aminophenol (MY 0510 from CIBA-GEIGY Corp.)	7.85
Epoxy silane (A-187 from UNION CARBIDE)	0.51
Aluminum powder	37.41
Silane treated Wollastonite (400 Wollastokup 10222 from NYCO)	21.00
Fumed silica (CABOSIL® M5 from Cabot Corp.)	2.04

Hardener Component

<u>Ingredient</u>	<u>Component (wt. %)</u>
p-aminodicyclohexylmethane	80.00
Amine adduct of MY 0500 (HY 355 from CIBA-GEIGY Corp.)	10.00
Dimethylaminopropaneamine	5.25
Tris(dimethylamino)phenol (DY 064 from CIBA-GEIGY Corp.)	3.00
Amino silane (silane A-1102 from UNION CARBIDE)	1.50
Fluoropolymer surfactant (FLUORAD® FC-430 from 3M Corp.)	0.25

The mix ratio of the epoxy resin component to the hardener component is 100/17 by weight.



Table 12

Lap Shear Strength

<u>-67°F</u> 1860 psi	<u>75°F</u> 3006 psi	<u>180°F</u> 2247 psi	<u>300°F</u> 1746 psi	<u>400°F</u> 455 psi
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ASTM D1002, 7 day/77°F cure

## Claims

1. A two component epoxy adhesive system comprising
  - (A) an epoxy component comprising:
    - (1) at least one aromatic multifunctional epoxy resin; and
  - (B) a hardener component comprising:
    - (1) a polyamide of a dimer fatty acid,
    - (2) at least one aliphatic or cycloaliphatic amine and
    - (3) at least one aromatic amine; and
 wherein a polyglycidyl ether of sorbitol, having more than 2 oxirane groups per molecule, as an accelerator is present in the epoxy component, a tertiary amine accelerator is present in the hardener component or both a polyglycidyl ether of sorbitol is present in the epoxy component and a tertiary amine accelerator is present in the hardener component.
2. A two component epoxy adhesive system according to claim 1 wherein said aromatic multifunctional epoxy resin is an aromatic epoxy resin containing on average at least two 1,2-epoxy groups per molecule.
3. A two component epoxy adhesive system according to claim 1 wherein said aromatic multifunctional epoxy resin is selected from the group consisting of N,N,N',N'-tetraglycidyl derivative of methylene dianiline, epoxidized novolaks, epoxidized Bisphenol A resins, epoxidized resorcinol epoxidized Bisphenol F and N,N,O-triglycidyl-4-aminophenol.
4. A two component epoxy adhesive system according to claim 1 wherein said aromatic multifunctional epoxy resin is N,N,O-triglycidyl-4-aminophenol.
5. A two component epoxy adhesive system according to claim 1 wherein said epoxy component further comprises an aliphatic multifunctional epoxy resin.
6. A two component epoxy adhesive system according to claim 5 wherein said aliphatic multifunctional epoxy resin is selected from the group consisting of diglycidylesters of cyclohexane-1,2-dicarboxylic acid, trimethylolethane triglycidyl ether and trimethylol propane triglycidyl ether.
7. A two component epoxy adhesive system according to claim 5 wherein said aliphatic multifunctional epoxy resin is trimethylol propane triglycidyl ether.
8. A two component epoxy adhesive system according to claim 1 wherein said polyamide of a dimer fatty acid is a hydrogenated polyaminoamide.
9. A two component epoxy adhesive system according to claim 1 wherein said aliphatic or cycloaliphatic amine is selected from the group consisting of monoethanolamine, N-aminoethyl ethanolamine, ethylenediamine, hexamethylenediamine, trimethylhexamethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, N,N-dimethylpropylenediamine-1,3, N,N-diethylpropylenediamine-1,3, bis(4-amino-3-methylcyclohexyl)methane, bis(p-aminocyclohexyl)methane, 2,2-bis(4-amino-cyclohexyl)propane, N-aminoethyl-piperazine, 1,2-diaminocyclohexane, 1,4-diaminocyclohexane, 1,3-bis(aminomethyl)cyclohexane, isophorone diamine, and 3,5,5-trimethyl-s-(aminomethyl)-cyclohexylamine.

10. A two component epoxy adhesive system according to claim 1 wherein said aliphatic or cycloaliphatic amine is selected from the group consisting of bis(p-aminocyclohexyl)methane, N,N-dimethylpropylene diamine-1,3, isophorone diamine and diethylenetriamine.
- 5 11. A two component epoxy adhesive system according to claim 1 wherein said aliphatic or cycloaliphatic amine is selected from the group consisting of N,N-dimethylpropylene diamine-1,3 and bis(p-aminocyclohexyl)methane.
- 10 12. A two component epoxy adhesive system according to claim 1 wherein said aromatic amine is selected from the group consisting of m-phenylene-diamine, p-phenylenediamine, bis(p-aminophenyl)methane, bis(p-aminophenyl)-sulfone, m-xylylenediamine, toluene diamine, 4,4'-methylene-dianiline, a diaminodiphenylether, benzidine, 4,4'-thiodianiline, 4-methoxy-6-m-phenyldiamine, 2,6-diaminopyridine, diansidine and 1-methyl-imidazole.
- 15 13. A two component epoxy adhesive system according to claim 1 wherein said aromatic amine is selected from the group consisting of m-xylylenediamine, 4,4'-methylene-dianiline and bis(p-aminophenyl)-sulfone.
14. A two component epoxy adhesive system according to claim 1 wherein said aromatic amine is selected from the group consisting of m-xylylenediamine and 4,4'-methylene-dianiline.
- 20 15. A two component epoxy adhesive system according to claim 1 wherein said epoxy component further comprises one or more fillers.
- 25 16. A two component epoxy adhesive system according to claim 1 wherein said epoxy component further comprises an epoxy silane as a adhesion promoter.
17. A two component epoxy adhesive system according to claim 1 wherein said tertiary amine accelerator is selected from the group consisting of triethylamine, tris(dimethylaminoethyl)phenol, boron trifluoride-amine complex, benzyl dimethylamine, and 2-dimethylaminomethyl)phenol.
- 30 18. A two component epoxy adhesive system according to claim 1 wherein said tertiary amine accelerator is tris(dimethylaminoethyl)phenol.
- 35 19. A two component epoxy adhesive system according to claim 1 wherein said hardener component further comprises a surfactant and one or more fillers.
- 40 20. A method of bonding or sealing two surfaces together comprising application of a two component epoxy adhesive system according to claim 1 to one or both surfaces to be bonded; placing the surfaces together with said adhesive system positioned therebetween and permitting the adhesive to cure at from about room temperature to about 121°C.